in the range (3–6) × 10^3 and appear to be characteristic of the unit Ta_6X_{12} with +2 charge. Because these two bands are independent of the halide they also must be associated with transitions involving only metal orbitals within the octahedral arrangement[6] of metal atoms. The positions of the remaining bands shift to lower energies in the order $Ta_6Cl_{12}^{2+} > Ta_6Br_{12}^{2+} > Ta_6I_{12}^{2+}$. A more detailed account of the spectra, magnetic susceptibilities, and chemical properties of these ions will be given in a subsequent paper.[16]

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The Equilibrium Phase Diagrams for the Tantalum–Tantalum Bromide and Tantalum–Tantalum Iodide Systems[1]

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The tantalum–tantalum bromide and the essential features of the tantalum–tantalum iodide system have been elucidated. In the bromide system four phases of composition lower than $TaBr_5$ were established, *viz.*, $TaBr_4$, $TaBr_{2.83}$, $TaBr_{2.5}$, and $TaBr_{2.33}$. By comparison the iodide system is very simple as evidenced by only the two lower phases TaI_4 and $TaI_{2.33}$. In the bromide system a eutectic occurs at 267° and the composition $TaBr_{4.87}$. The $TaBr_4$ melts incongruently at 392° to form liquid of composition near $TaBr_{4.85}$ and the next lower solid $TaBr_{2.83}$. Equilibrations of $TaBr_4$ at a series of temperatures above 400° established that $TaBr_{2.83}$ melts incongruently within the interval 447–453° to form bromine-rich liquid and the phase $TaBr_{2.5}$. Similarly it was determined that $TaBr_{2.5}$ melts incongruently to form $TaBr_{2.33}$ in the interval 671–680°. Exact location of the melting temperatures for the bromides with $Br/Ta < 4$ was hindered by the very sluggish reactions. That $TaBr_{2.33}$ was the lowest phase in the system was established by equilibrations of the higher halides with tantalum at temperatures up to 750°; a melting point for $TaBr_{2.33}$ was not observed. In the iodide system the melting point of TaI_5 occurred at 382°, with a eutectic at 365° and the composition $TaI_{4.87}$. Decomposition of TaI_4 into iodine-rich liquid and $TaI_{2.33}$ occurred in the interval 395–402° at a very low rate. Equilibrations of $TaI_{2.33}$ and Ta up to 815° provided no evidence for any new phases. Both $TaBr_{2.33}$ and $TaI_{2.33}$ provide aqueous solutions of the ions $Ta_6Br_{12}^{2+}$ and $Ta_6I_{12}^{2+}$. Hence these compounds are formulated correctly as $(Ta_6Br_{12})Br_2$ and $(Ta_6I_{12})I_2$. The chemical properties and stoichiometry of the phases $TaBr_{2.5}$ and $TaBr_{2.83}$ suggest that they should be formulated as $(Ta_6Br_{12})Br_3$ and $(Ta_6Br_{12})Br_5$, respectively.

Introduction

In previous work in this laboratory[2] it was found that the polynuclear halides $(Ta_6Br_{12})Br_2$ and $(Ta_6I_{12})I_2$ could be prepared *via* aluminum reduction of the respective tantalum(V) halides. But the question whether or not these compounds were equilibrium compounds in the tantalum–tantalum halide systems was not answered. Other workers have obtained aqueous solutions of the polynuclear tantalum halides *via* reduction of the tantalum(V) halides with sodium,[3] aluminum,[4,5] or lead,[6,7] followed by extraction of the products into water. However, these workers did not successfully identify the anhydrous phase giving rise to these solutions.

More recently Schäfer, *et al.*, have prepared the lower halides $TaCl_3$,[8] $TaCl_{2.5}$,[8] $TaBr_3$,[9] $TaBr_{2.5}$,[9,10] and $TaI_{2.33}$[10] by means of chemical transport reactions. The compounds $TaCl_{2.33}$ and $TaBr_{2.33}$ were not observed in their work.[9] In order to clarify the question about the number of reduced halides in the tantalum–tantalum halide systems this work was undertaken. Because excessive pressures were encountered in sealed tube equilibrations at high temperatures in the tantalum chloride system, a detailed investigation of the tantalum bromide and iodide systems was undertaken first.

Experimental

Materials.—The tantalum(V) halides were prepared by direct combination of the elements at elevated temperatures in sealed, evacuated tubes. Subsequent handling of these and other reactive materials was always done on a high vacuum line or in the glove box. The glove box was filled with argon maintained at a dew point of *ca.* −75°.

Tantalum(IV) Bromide.—After some exploratory work it was found that large amounts of $TaBr_4$ were most conveniently prepared by aluminum reduction of $TaBr_5$ at 250°. In a typical preparation 0.2 g. of aluminum foil and 15 g. of $TaBr_5$ were placed in a Pyrex tube which was *ca.* 35 cm. long with a constriction located about one-third of the distance from the end containing the reaction mixture. The tube was evacuated, sealed, placed in a furnace with the end containing the aluminum foil lowered from the horizontal, and heated to 250°. After 7 days the reaction was complete and a dark crystalline solid was obtained. Excess $TaBr_5$ and product $AlBr_3$ were removed by sublimation at 225° for 16 hr. leaving the desired $TaBr_4$ as residue.

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[1] Contribution No. 1639. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

[2] (a) R. E. McCarley, P. J. Kuhn, and B. G. Hughes, Abstracts, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964, p. 36L; (b) P. J. Kuhn and R. E. McCarley, *Inorg. Chem.*, **4**, 1482 (1965).

[3] W. H. Chapin, *J. Am. Chem. Soc.*, **32**, 323 (1910).

[4] O. Ruff and F. Thomas, *Ber.*, **55**, 1466 (1922).

[5] O. Ruff and F. Thomas, *Z. anorg. allgem. Chem.*, **148**, 1 (1925).

[6] K. Lindner and H. Feit, *Ber.*, **55**, 1458 (1922).

[7] K. Lindner and H. Feit, *Z. anorg. allgem. Chem.*, **137**, 66 (1924).

[8] H. Schäfer, H. Scholz, and R. Gerken, *ibid.*, **331**, 154 (1964).

[9] H. Schäfer, R. Gerken, and H. Scholz, *ibid.*, **335**, 96 (1965).

[10] H. Schäfer, D. Bauer, W. Beckman, R. Gerken, H. G. Nieder-Vahrenholz, K. J. Niehus, and H. Scholz, *Naturwissenschaften*, **51**, 241 (1964).

Analytical data for products from three different preparations are given below.

Anal. Calcd. for $TaBr_4$: Ta, 36.15; Br, 63.85. Found, No. 1: Ta, 36.27, 36.37; Br, 63.23, 63.18. No. 2: Ta, 36.24, 36.23; Br, 63.42. No. 3: Ta, 36.39, 36.38; Br, 63.52, 63.47.

The properties and diffraction pattern of this material agreed with those reported previously.[11] Yields were virtually quantitative based upon the amount of aluminum used. A small excess of $TaBr_5$ was always used in each reaction to ensure that the aluminum was completely consumed and to avoid formation of lower tantalum bromides.

Tantalum(IV) Iodide.—The technique described above for $TaBr_4$ was applied to the preparation of TaI_4 with only slight modification. Because it was not possible to remove excess TaI_5 from TaI_4 without causing some decomposition of the latter, the reaction was carried out using exact stoichiometric quantities of TaI_5 and aluminum, according to eq. 1.

$$3TaI_5 + Al = 3TaI_4 + AlI_3 \qquad (1)$$

In a typical reaction 0.25 g. of aluminum foil and 23.0 g. of TaI_5 were maintained at 325° for 6 days. Subsequently AlI_3 was removed by sublimation at 250° and the tube opened in the drybox. Material prepared in this manner hydrolyzed rapidly and completely in aqueous solution to produce the brown oxide characteristic of tantalum(IV) on addition of aqueous ammonia.

Anal. Calcd. for TaI_4: Ta, 26.29; I, 73.71. Found: Ta, 26.10, 25.88; I, 73.78, 73.96; I/Ta, 4.06 (average).

Dodeca-μ-iodo-hexatantalum Diiodide.—This compound, henceforth designated as $TaI_{2.33}$ or $(Ta_6I_{12})I_2$, was produced according to the method reported by McCarley, Kuhn, and Hughes.[2]

Anal. Calcd. for $(Ta_6I_{12})I_2$: Ta, 37.93; I, 62.07; I/Ta, 2.33. Found: Ta, 38.37; I, 61.42; I/Ta, 2.28.

X-Ray powder diffraction data for this compound are given in Table I. The compound dissolved in water to produce a green solution characteristic of the ion[2] $Ta_6I_{12}^{2+}$.

Dodeca-μ-bromo-hexatantalum Dibromide.—Subsequently this compound will be designated as $TaBr_{2.33}$ or $(Ta_6Br_{12})Br_2$. It was also prepared by aluminum reduction of the pentahalide.[2]

Anal. Calcd. for $(Ta_6Br_{12})Br_2$: Ta, 49.25; Br, 50.75; Br/Ta, 2.33. Found: Ta, 49.16, 49.39; Br, 50.63, 50.57; Br/Ta, 2.33, 2.34.

X-Ray powder diffraction data for this compound are given in Table I. This material dissolved in water readily to give a deep green solution characteristic of the $Ta_6Br_{12}^{2+}$ ion.[2]

Analytical Procedure.—All samples were placed in screw-cap vials in a drybox for weighing and then transferred rapidly to beakers containing a dilute aqueous ammonia solution for hydrolysis. The sample vials were weighed initially with the sample under argon, and finally the empty bottle was weighed filled with air. A negative bouyancy correction was applied to the apparent sample weight because of the initial weighing under argon.

Tantalum was determined gravimetrically as the oxide Ta_2O_5 after hydrolysis of the sample. For the lower halides prolonged heating near the boiling point (2–6 hr.) was necessary to effect complete hydrolysis. The solutions were cooled to room temperature, acidified with dilute nitric acid to pH 1, and filtered on medium retention paper, and the precipitate was washed thoroughly with dilute nitric acid. Halogens were subsequently determined in the filtrate solution.

An uncertainty of ±0.02 in the halogen-to-tantalum ratio is estimated for all numbers reported, unless otherwise noted.

X-Ray Diffraction Data.—X-Ray data were obtained with a 114.59-mm. Debye–Scherrer camera using Ni-filtered Cu Kα radiation. Finely-powdered samples were hermetically sealed in 0.2-mm. Lindemann glass capillaries. Corrections for absorption and film shrinkage were not applied. Exposure times varied from 16 to 24 hr. depending upon the sample. Relative intensities of lines were estimated visually by comparison with the most intense line.

Phase Studies.—Thermal analysis, differential thermal analysis, and isothermal equilibrations were employed for the construction of the equilibrium phase diagrams. Because many of the reactions were extremely sluggish, particularly those involving the halides of Br/Ta less than 4, some equilibration reactions required up to 2 weeks to reach equilibrium. Hence, because of the time and labor involved, some of the important temperatures were established only within a limit of ±5°.

Samples for thermal analysis were sealed in evacuated and outgassed 11 mm. o.d. × 50 mm. Pyrex or Vycor tubing, which contained a 3-mm. i.d. well sealed in one end for location of the measuring thermocouple. All samples were sufficiently large so that the thermocouple well was completely covered by the sample. The desired composition for each mixture was obtained by combining accurately weighed samples of compounds of known composition. In particular it was found that only samples in the composition range $TaBr_{4-5}$ and TaI_{4-5} gave useful thermal analysis data. These samples were prepared from the pure components TaX_5 and TaX_4 and equilibrated at a temperature below the established decomposition temperature of the TaX_4 before running the first heating or cooling curve.

The thermal analyses were performed with the samples located in a 12-in. Marshall furnace which was fitted with transite end covers to reduce heat loss. The sample cell was set into a slot drilled into a porous dolomitic insulating block, which in turn was contained in a copper block to smooth out temperature gradients. Holes were drilled up through the copper and insulating brick to accommodate the measuring thermocouples, one of which fit into the well in the sample cell. Sample temperature and the differential temperature relative to the dolomitic insulating block were registered on a two-pen recorder equipped with variable span and suppression on the temperature pen. The furnace temperature was regulated by a proportioning controller with its thermocouple in contact with the inside wall of the furnace. Heating and cooling rates of 2–3° min.$^{-1}$ were generally employed. The uncertainty of all temperatures established by thermal analysis is estimated not to exceed 2°.

Equilibration Experiments.—Because of the sluggish reactions involving the lower tantalum halides it was necessary to establish some of the equilibrium phases by long-term (in some cases up to 14 days) equilibration of samples at a series of temperatures, followed by analysis and procurement of X-ray diffraction data. Samples for this purpose were sealed in Pyrex or Vycor capsules and heated in a 12-in. Marshall furnace, where the temperature was controlled to within ±1°.

To establish the lowest halide phase, samples of the higher halides were sealed in 0.12-in. tantalum tubing. These tubes were prepared by closing one end of a 3-in. section of tubing by arc melting under helium, introducing the sample (in a drybox), and sealing the open end by crimping with pliers. The tantalum capsule was then sealed in a Vycor tube under *ca.* 600 mm. of argon.

Equilibrations which did not involve reaction with the metal were carried out in Vycor tubing under *ca.* 600 mm. of argon if temperatures greater than 600° were required. The argon greatly reduced the rate of attack of the tantalum halide vapors on the glass walls. Where only X-ray diffraction data were needed small samples similarly were sealed in 2-mm. i.d. capillary tubing.

Results

The phase diagrams for the tantalum–tantalum bromide and tantalum–tantalum iodide systems are given in Figures 1 and 2, respectively. The evidence leading to the establishment of the transformation temperatures and identity of the phases in each system is outlined below.

The $TaBr_5$–$TaBr_4$ Region.—Thermal analysis of samples in the range $TaBr_5$–$TaBr_4$ established the following features: $TaBr_5$, m.p. 272°; eutectic at Ta-

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[11] R. E. McCarley and J. C. Boatman, *Inorg. Chem.*, **2**, 547 (1963).

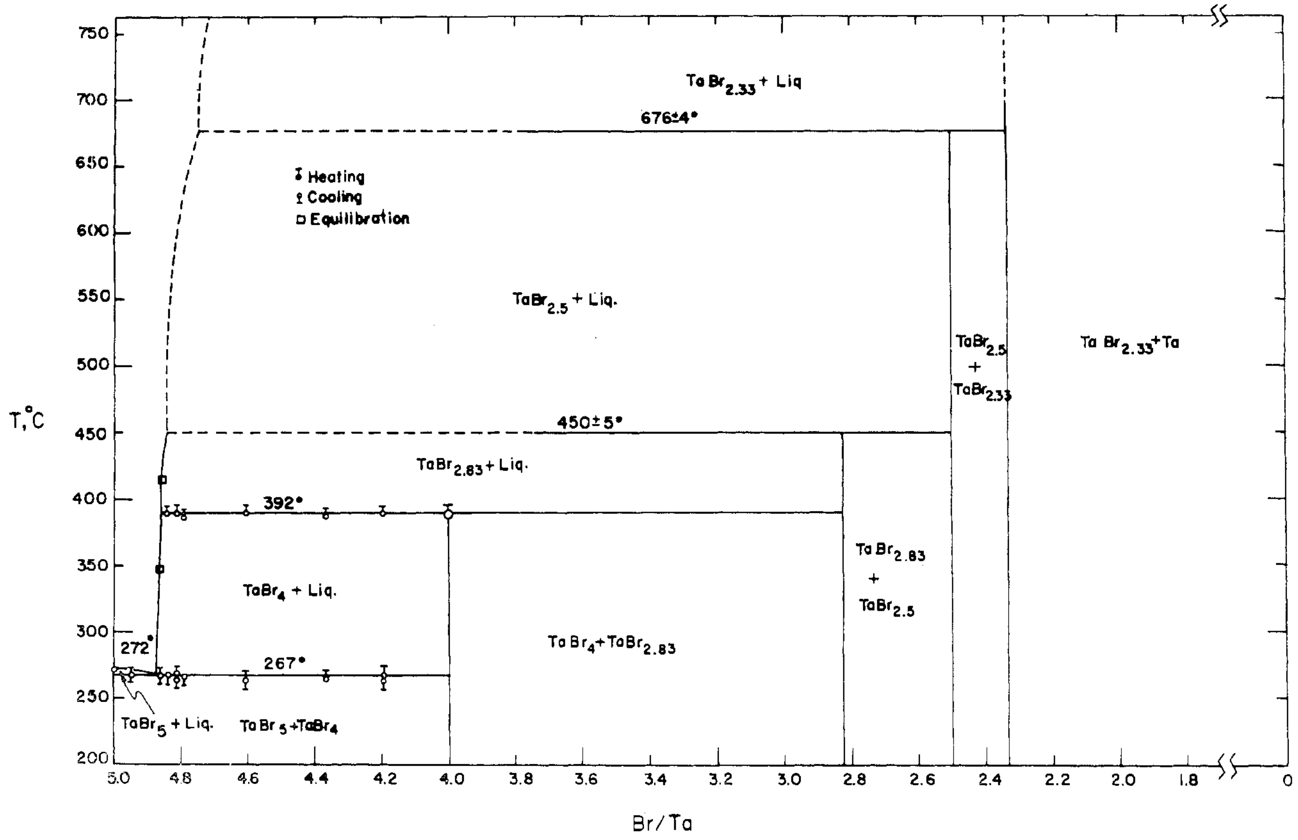

Figure 1.—The $TaBr_5$–Ta phase diagram.

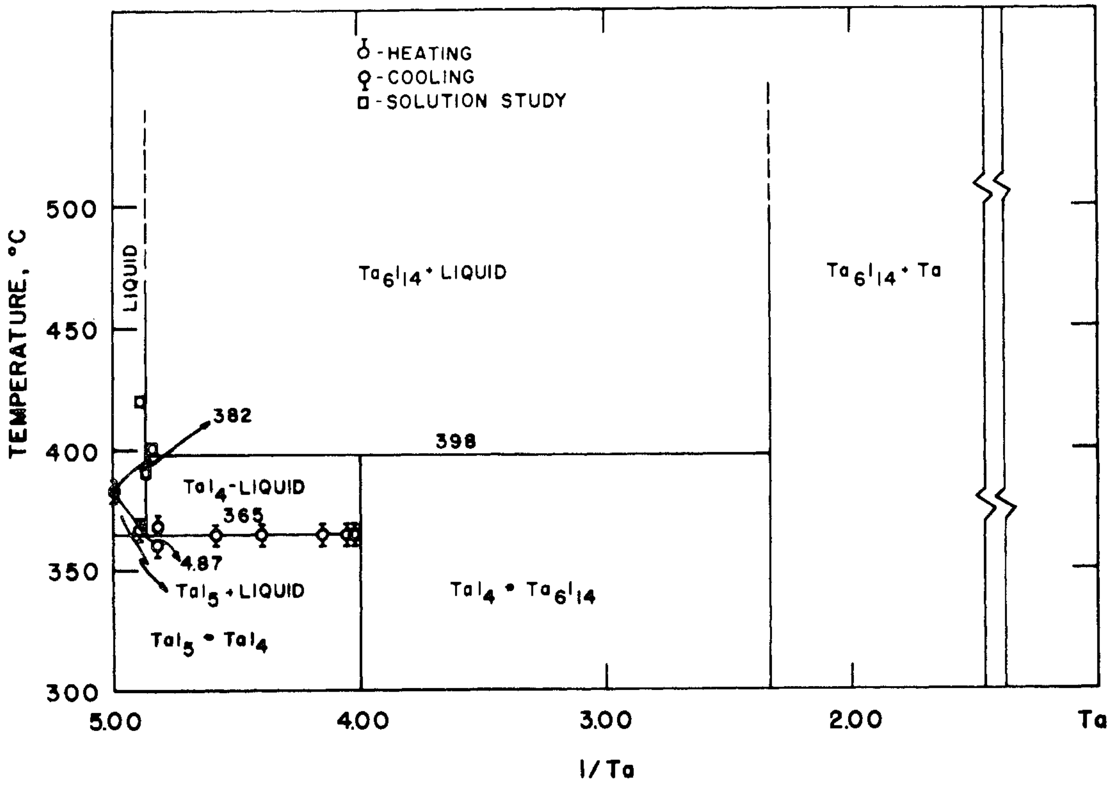

Figure 2.—The TaI_5–Ta phase diagram.

$Br_{4.87\pm0.02}$, m.p. 267°; and $TaBr_4$, m.p. 392° dec. The melting point of $TaBr_5$ was reproduced on repeated runs on several different samples of doubly-sublimed material. Values of 280°[12] and 265°[13] had been reported previously for the melting point of $TaBr_5$; the former value was obtained from vapor pressure measurements.

All mixtures in this region exhibited a thermal arrest at the eutectic temperature, but only samples from $TaBr_5$ to $TaBr_{4.84}$ exhibited an arrest at 392°. Equilibration of a mixture of $TaBr_5$ and excess $TaBr_4$ at 350°, followed by filtration and analysis of the liquid, established a liquidus composition of $TaBr_{4.87}$. The composition of $TaBr_{4.87}$ at the eutectic was obtained from the intersection of the liquidus line (which appeared to be essentially vertical) with the eutectic horizontal.

The arrest at 392° was observed only on heating. Cooling of samples in this region, even if equilibrated several hours above 392°, showed only the arrest at 267°. Evidence cited below indicates that equilibration between the lower halides and $TaBr_5$ is so sluggish that the thermal arrest at 392° should not be observed on cooling. Above 392° decomposition of $TaBr_4$ results in formation of $TaBr_{2.83}$ and liquid of composition near $TaBr_{4.85}$ (actually found for the liquid equilibrated with $TaBr_4$ at 420°).

Observations on $TaBr_{2.83}$.—Samples of $TaBr_4$ equilibrated for 1, 2, and 3 days at 435° afforded solids having Br/Ta of 3.01, 2.88, and 2.84, respectively, after removal of $TaBr_5$ at 225°.[14] The product from a larger sample of $TaBr_4$, which was equilibrated at 426° for 10 days, possessed a composition of $TaBr_{2.82}$ and gave a unique X-ray powder pattern corresponding to the data for this phase in Table I.

Though equilibrium decomposition of $TaBr_4$ above 392° is slow, the reverse reaction below 392° to form $TaBr_4$ is evidently so slow that reaction is not observed. A mixture of $TaBr_5$ and $TaBr_{2.83}$ equilibrated for 13 days at 375° followed by removal of unreacted $TaBr_5$ at 225°[14] gave no evidence for formation of $TaBr_4$. An X-ray pattern of the product showed no lines other than those of $TaBr_{2.83}$. Thus, as noted above, failure to observe an arrest at 392° on cooling mixtures in the region Br/Ta = 4–4.8 is not surprising.

On the other hand, equilibration of either $TaBr_{2.5}$ or $TaBr_{2.33}$ with $TaBr_5$ at 435° led directly to formation of $TaBr_{2.83}$, albeit slowly. A similar reaction performed at 375° also terminated in formation of $TaBr_{2.83}$, which again illustrated the hindered formation of $TaBr_4$ from the lower halides.

The pure $TaBr_{2.83}$ is brown and dissolves in water with production of a green solution characteristic of the ion $Ta_6Br_{12}^{2+}$. Further work on the chemistry of this compound is in progress. A series of equilibrations at 447–470° fixed the incongruent melting of $TaBr_{2.83}$ at 450 ± 5°; the solid $TaBr_{2.5}$ and liquid of higher composition result from the process.

TABLE I

MOST INTENSE LINES IN X-RAY POWDER PATTERNS OF SOME LOWER TANTALUM HALIDES

$TaBr_{2.83}$ d, Å.	$TaBr_{2.5}$ d, Å.	$TaBr_{2.33}$ d, Å.	$TaI_{2.33}$ d, Å.
9.38 (10)[a]	7.55 (10)[a]	7.39 (10)[a]	8.02 (10)[a]
6.59 (10)	3.32 (5)	7.03 (6)	3.23 (3)
4.65 (5)	2.89 (10)	6.59 (8)	3.14 (8)
4.23 (5)	2.55 (10)	3.51 (10)	2.95 (5)
4.11 (5)	2.47 (10)	3.00 (7)	2.61 (10)
3.57 (8)	2.30 (10)	2.86 (9)	2.37 (3)
2.97 (7)	2.24 (10)	2.74 (5)	2.29 (3)
2.61 (10)	2.15 (5)	2.66 (6)[b]	2.22 (3)
2.55 (9)	2.11 (4)	2.49 (6)[b]	2.09 (3)
2.44 (9)	2.09 (4)	2.42 (10)	2.06 (3)
2.40 (9)	1.841 (7)	2.36 (5)	2.04 (3)
2.33 (8)	1.814 (6)	2.25 (5)	2.01 (4)
2.27 (8)	1.740 (4)	2.20 (5)	1.886 (3)
2.25 (8)	1.307 (3)	1.914 (5)[b]	1.817 (3)
2.11 (6)	1.297 (3)	1.866 (5)[b]	1.776 (3)
2.04 (6)	1.219 (4)	1.760 (5)	1.618 (5)
2.02 (7)	1.204 (4)	1.660 (5)[b]	1.572 (3)
1.777 (5)	1.181 (4)	1.498 (5)	1.308 (3)

[a] Relative intensities as estimated visually are given in parentheses. [b] Unusually broad lines.

Experiments on $TaBr_{2.5}$.—The composition of the next lower phase below $TaBr_{2.83}$ was bracketed by equilibration of $TaBr_{2.33}$–$TaBr_5$ mixtures having Br/Ta ratios in the range 2.38–3.00 at 500°. Only lines of the new phase could be identified in X-ray patterns of the products from the mixtures in the Br/Ta range 2.5–3.0. Because it had been observed that this phase was not reduced by tantalum metal below *ca.* 640°, the final composition of the pure solid was determined from the product obtained from reaction of $TaBr_{2.83}$ with Ta at 606° for 2 days.

Anal. Calcd. for $TaBr_{2.5}$: Ta, 47.5. Found: Ta, 47.2, 47.4.

The X-ray powder pattern of this compound is practically identical with that of $TaCl_{2.5}$,[8] a point previously noted by Schäfer, *et al.*,[9] who identified this compound as a product of a transport reaction between $TaBr_5$ and Ta under appropriate conditions. X-Ray diffraction data for $TaBr_{2.5}$ are given in Table I.

Equilibrations Involving $TaBr_{2.5}$ and $TaBr_{2.33}$.—Whereas reduction of $TaBr_{2.5}$ with tantalum did not proceed measurably below *ca.* 640°, above this temperature formation of $TaBr_{2.33}$ did occur. Thus incongruent melting of the $TaBr_{2.5}$ at *ca.* 640° was suspected as providing the mechanism for reduction. This was verified subsequently by equilibration of $TaBr_{2.5}$ in the absence of metal at 10° intervals in the range 620–680° for 1–3 days, which established the incongruent melting at 676 ± 4°. The solid phase resulting from this process was $TaBr_{2.33}$, as confirmed by both analysis and X-ray powder pattern; however, the composition of the liquid at this point was not determined.

That $TaBr_{2.33}$ is the lowest halide in this system was established by equilibrations of both $TaBr_{2.5}$ and Ta-

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(12) K. M. Alexander and F. Fairbrother, *J. Chem. Soc.*, S223 (1949).

(13) E. L. Wiseman and N. W. Gregory, *J. Am. Chem. Soc.*, **71**, 2344 (1949).

[14] At 225° the vapor pressure of $TaBr_5$ is estimated to be only 12 mm.[11] Because of either the extremely low reaction rates or very low decomposition pressures none of the compounds $TaBr_4$, $TaBr_{2.83}$, or $TaBr_{2.33}$ was found to decompose *in vacuo* at 225°. Hence this temperature was considered safe for separating $TaBr_5$ from the lower phases by sublimation *in vacuo*.

$Br_{2.33}$ sealed in tantalum tubing at temperatures up to 750°. No evidence for a phase lower than $TaBr_{2.33}$ was found, nor was any homogeneity range in $TaBr_{2.33}$ evident from the X-ray diffraction patterns. X-Ray data for $TaBr_{2.33}$ as given in Table I are in good agreement with data obtained on this compound produced by aluminum reduction.[2]

Results on the Tantalum–Tantalum Iodide System.—Repeated runs on each of several samples of resublimed TaI_5 gave halts at the melting point of $382 \pm 2°$; no other thermal event was detected. A melting point of 496° was previously estimated[12] from vapor pressure data, but a distinct discontinuity in the pressure–temperature plot was not observed. It seems likely that the TaI_5 was liquid over the complete range of the vapor pressure measurements.

All samples in the range TaI_5–TaI_4 gave thermal arrests at $365 \pm 2°$, the eutectic temperature. Körösy[15] had previously reported the same temperature for the melting point of pure TaI_5. A second arrest on heating to *ca.* 420° was found only for samples of composition near TaI_4, but the temperature was not reproducible. Equilibrations of TaI_4 in liquid TaI_5 followed by filtration and analysis of the liquid established a liquidus composition of $TaI_{4.87 \pm 0.02}$ at 390, 400, and 420°. Thus the liquidus line is nearly vertical and intersects the eutectic horizontal at $TaI_{4.87}$, the eutectic composition.

From X-ray powder patterns it was deduced that TaI_4 decomposes into $TaI_{2.33}$ and liquid near $TaI_{4.87}$ when heated above about 400°. Three-day equilibration of samples at five temperatures in the range 395–428° established the incongruent melting point at 398° (with an uncertainty of *ca.* 3°). The powder pattern of $TaI_{2.33}$ resulting from equilibration of TaI_4 above 398° is in complete agreement with that given by $TaI_{2.33}$ resulting from aluminum reduction; the data are given in Table I.

Equilibration of $TaI_{2.33}$ in tantalum tubing at 815° provided no evidence for other lower iodides, nor for any change in composition of the $TaI_{2.33}$ phase.

Discussion

Tantalum–Tantalum Bromide System.—The results reported above are noteworthy not only because of the number and unusual stoichiometry of the phases found, but also because of the absence of evidence for certain phases which reasonably might have been expected. Also the properties of these compounds are of great interest because of the evidence of metal–metal bonding and polynuclear ion formation which they present.

Although the preparation of $TaBr_4$ has been reported previously,[9,11] the method given in the Experimental section is far superior to that reported earlier if larger amounts of the compound are desired. Metal–metal bonding is probably an important feature in the structure of $TaBr_4$ (and related tetrahalides[16]) as evidenced by its diamagnetism.[11] Such metal–metal bonding and the consequent polymeric character of the solid may be responsible for the very sluggish reactions observed for both $TaBr_4$ and TaI_4. The latter compound has been reported to be isostructural with α-NbI_4, the structure of which does involve metal–metal bonding in pairs of adjacent metal atoms.[17]

The failure to observe the formation of $TaBr_4$ after a 13-day equilibration of $TaBr_5$ and $TaBr_{2.83}$ at 375° is regarded as a result of a kinetically hindered reaction, and not lack of evidence for the thermodynamic reversibility of the reaction occurring at the peritectic temperature, 392°. We suggest the following hypothesis to correlate this observation with others noted in the results.

Because the compound $TaBr_{2.83}$ dissolves in water giving the ion $Ta_6Br_{12}{}^{2+}$, it is probable that the unit Ta_6Br_{12} is present in the solid phase. The formula $(Ta_6Br_{12})Br_5$ indicates this. In aqueous solution the Ta_6Br_{12} unit can be oxidized[18] to an ion of charge 4+, and compounds of $Ta_6Br_{12}{}^{4+}$ have been prepared.[19] Accepting this as evidence that the Ta_6Br_{12} unit may exist in several different charge states we also formulate $TaBr_{2.5}$ and $TaBr_{2.33}$ as $(Ta_6Br_{12})Br_3$ and $(Ta_6Br_{12})Br_2$, respectively. Transformations between solids containing the units in different charge states are slow, but transformation from $TaBr_{2.83}$ to $TaBr_4$ is effectively prevented because disruption of the Ta_6Br_{12} unit is required.

It is surprising that no evidence was obtained in this work for inclusion of a $TaBr_3$ phase in the equilibrium diagram. Schäfer, *et al.*,[9] have prepared this compound *via* vapor phase transport and found it to be related in structure[20] and extensive homogeneity range [8,21,22] to the analogous $TaCl_3$, $NbCl_3$, and $NbBr_3$. That $TaBr_{2.83}$ does not possess the trihalide structure is evidenced by its facile reaction with water to produce $Ta_6Br_{12}{}^{2+}$. Also, peritectic decomposition of $TaBr_4$ should lead to a composition at the upper limit of the homogeneity range if the trihalide phase were formed. Finally, an authentic sample of $TaBr_3$ was prepared by the published method[9] and found to be a distinctly unique phase. A similar anomalous relationship between NbI_3[23] and the niobium–niobium iodide system has been noted by Seabaugh and Corbett.[24]

Finally, in this system the phase of lowest composition is the polynuclear $(Ta_6Br_{12})Br_2$, which evidently had been obtained by other investigators but never identified except in aqueous solution. The $(Ta_6Br_{12})Br_2$ is most conveniently prepared *via* aluminum reduction[2] of $TaBr_5$ because reactions of the higher bromides with tantalum are very slow. Detailed reports of the chemistry of $(Ta_6Br_{12})Br_2$, and the related $(Ta_6Cl_{12})Cl_2$ and $(Ta_6I_{12})I_2$, are forthcoming.[18,19]

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The Tantalum–Tantalum Iodide System.—The outstanding feature of this system is its simplicity. Yet some comments are necessary in order to clarify previously reported observations on the tantalum iodides. This work establishes that TaI_4 and $(Ta_6I_{12})I_2$ are the only equilibrium phases in the system. The latter compound provides the green aqueous solutions which were attributed to a subiodide corresponding to TaI_4,[25] and which Körösy[15] had obtained from solids having a composition in the range $TaI_{2.75}$–$TaI_{2.45}$. As noted under Results pure TaI_4 does not produce green aqueous solutions; rather it hydrolyzes to yield the hydrated, brown tantalum(IV) oxide. It is difficult to obtain TaI_4 in a state entirely free of either TaI_5 or $(Ta_6I_{12})I_2$. The method of preparation of TaI_4 used in this work, while satisfactory for purposes reported here, probably left some TaI_5 in the product. At the temperatures necessary to separate TaI_5 by sublimation (*ca.* 350°) some decomposition of TaI_4 may result. The product TaI_3, previously reported by us[11] as resulting from the reduction of TaI_5 with tantalum, can be accounted for in terms of a mixture of TaI_4 and $(Ta_6I_{12})I_2$.

There is a striking contrast between the lower phases present in the niobium iodide and tantalum iodide systems. In the equilibrium niobium iodide system only NbI_4 and Nb_3I_8 were identified[24] with NbI_3 occupying an anomalous position. Thus there is little apparent resemblance between the two systems in the lower phase region. It is possible, however, that Nb_3I_8 may have the polynuclear structure and be formulated as $(Nb_6I_{12})I_4$. Evidence has been obtained that indicates the related anhydrous phases $(Nb_6Cl_{12})Cl_2$ and $(Nb_6Br_{12})Br_2$ do exist[26] and that the ion $Nb_6Cl_{12}^{2+}$ can be oxidized to $Nb_6Cl_{12}^{4+}$ in aqueous solution.[18]

(25) R. F. Rolsten, *J. Am. Chem. Soc.*, **80**, 2952 (1958).

(26) R. E. McCarley, P. B. Fleming, and L. A. Mueller, to be published.

Notes

CONTRIBUTION FROM THE INSTITUTE FOR
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The Two-Electron Oxidation of Metal Atom Cluster Species of the Type $[M_6X_{12}]^{2+}$

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The oxidation–reduction behavior of metal atom cluster species, such as $[Ta_6X_{12}]^{2+}$, $[Nb_6X_{12}]^{2+}$, and $[Mo_6X_8]^{4+}$, under circumstances in which the cluster remains intact, are of interest for various reasons. Of particular pertinence to the question of chemical bonding in the clusters is the question of the extent and the ease with which the Nb and Ta species mentioned may be oxidized. A recently published molecular orbital treatment[2] of the $[Mg_6X_{12}]$ systems led to the result that the highest filled bonding MO is an A_{2u} level. When it is noted that this level is not very strongly bonding and that in a solvent such as water an increase in over-all charge from +2 to +4 should result in additional energy of solvation, a two-electron oxidation of $[M_6X_{12}]^{2+}$ leading to a diamagnetic product, $[M_6X_{12}]^{4+}$, might be expected to proceed at a relatively low potential. Conversely, the observation of such a process might be taken to substantiate, in some degree, the correctness of the order of molecular orbitals.

Oxidation reactions of the kind described have been observed for both the $[Nb_6Cl_{12}]^{2+}$ and the $[Ta_6X_{12}]^{2+}$ (X = Cl or Br) ions. In the case of the latter solid compounds such as the sulfates have been isolated.

Experimental

Standard Solutions of Dodeca-μ-halo-hexatantalum Sulfate.—Aqueous solutions of the $[Ta_6X_{12}]^{2+}$ halides were passed through a 2 cm. × 30 cm. column of strong anion-exchange resin, Amberlite IRA-401, in the sulfate form. After discarding the first 50 ml., the eluate was collected in a 250-ml. volumetric flask and diluted to the mark. The solutions were standardized by analyzing aliquots for tantalum and halide. Ratios of halide to tantalum for various solutions ranged from 1.97 to 2.00.

Titration of the $[Ta_6X_{12}]^{2+}$ Standard Solutions.—Oxidation–reduction titrations of the $[Ta_6X_{12}]^{2+}$ solutions were carried out indirectly using iron(III) ammonium sulfate solution as the oxidant and back titrating the iron(II) formed with standard ammonium tetrasulfatocerate(IV) solution. Aliquots of the standard, ion-exchanged solutions were added directly to excess iron(III) solution or passed through a Jones reductor into excess iron(III) solution. It was necessary to filter and wash the insoluble sulfate which formed on oxidation of the $[Ta_6X_{12}]^{2+}$ solutions in order to keep it from interfering with the subsequent titration.

Sulfate Derivatives of $[Ta_6X_{12}]^{4+}$.—An aqueous solution of $[Ta_6Cl_{12}]^{2+}$ acidified with sulfuric acid was oxidized with chlorine gas or iron(III) sulfate solution. The insoluble red-brown product was filtered, washed with ethanol and ether, and air dried.

Anal. Found: Ta, 59.23; Cl, 22.62; SO_4, 9.07; Cl/Ta, 1.95; SO_4/Ta, 0.288.

In a similar way, an aqueous solution of $[Ta_6Br_{12}]^{2+}$ acidified with sulfuric acid was oxidized with bromine water or iron(III) sulfate solution. The chocolate-brown precipitate was washed with ethanol and ether and air dried.

Anal. Found: Ta, 45.67; Br, 39.24; SO_4, 7.08; Br/Ta, 1.95; SO_4/Ta, 0.292.

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[2] F. A. Cotton and T. E. Haas, *Inorg. Chem.*, **3**, 10 (1964); there is a typographical error in Figure 3 of this paper. The lower $T_{2g}(xz,yz)$ level is actually $T_{1g}(xz,yz)$.